

## DISTRIBUTION OF PARTICULATE TRACE METALS IN THE WESTERN BAY OF BENGAL

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### ABSTRACT

Samples from 24 stations comprising inshore and offshore of the western Bay of Bengal have been analysed for particulate trace metals, total suspended matter (TSM) and particulate organic carbon (POC). The results show relative enrichment of particulate Mn, Fe, Cu, Zn, Pb and POC in inshore and particulate Ni and Cd in offshore regions. While relative enrichment of the former is attributed to river run-off, that of the latter is accounted for authigenic removal/scavenging. [On the other hand] the concentration levels of particulate Co and TSM are almost similar in both inshore and offshore regions. The vertical profiles showed a decreasing trend from surface to intermediate depths (200-500 m) followed by a slight increase in the bottom in the case of particulate Mn, Zn, Co, TSM and POC while a continuous increase from surface to bottom in the case of Fe, Ni, which appeared to be related to a combination of factors such as authigenic precipitation/scavenging, resuspension of bottom rich sediments, and diffusion followed by precipitation at sediment-water interface. On the other hand, the vertical profiles of Cu revealed a continuous decrease from surface to bottom indicating either its removal from TSM by desorption or its regeneration in dissolved form at sediment-water interface due to early diagenesis. Based on the distribution pattern and correlation matrix, possible sources (terrigenous, hydrogenous and biogenous) of their occurrence have been identified. The average concentration levels of particulate trace metals obtained in the present study broadly agree with those of earlier reports on Bay of Bengal, Andaman Sea, and Indian Ocean. However, variations in case of particulate Mn, Fe, Zn and Pb are attributed to differences in river runoff, and nature and composition of TSM.

*Key- Words:* Particulate trace metals, TSM, POC, Western Bay of Bengal.

### INTRODUCTION

Marine particulate matter is of considerable geochemical importance since it acts as a carrier phase for the transport of chemical constituents from sea water to the bottom sediments. Factors such as production, sinking and decomposition of particulate matter control to a large extent, the recycling and distribution of trace elements within the oceans. This recycling involves uptake of dissolved trace elements by particulate phases and their subsequent regeneration when the latter undergoes oxidation and/or dissolution either within the water column or within the surficial sediments with subsequent diffusion into the water column (Bruland, 1983).

Though there are several reports on the average concentration levels of dissolved and particulate trace metals in the Indian seas namely, the Arabian sea (Sen Gupta, Singbal and Sanzgiri, 1978), Laccadive Sea (Sanzgiri and Moraes, 1979), Bay of Bengal

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(Jegatheesan and Venugopalan, 1973; Braganca and Sanzgiri, 1980; Rajendran, De Sousa and Reddy, 1982; Satyanarayana, Prasada Reddy, Dileepkumar and Ramesh, 1987), and Andaman Sea (Sanzgiri and Braganca, 1981), most of these studies do not provide information on the interaction of trace elements with particulate matter. The present study deals with the distribution of particulate trace metals (Fe, Mn, Co, Ni, Cu, Pb, Zn and Cd) and their possible interactions with total suspended matter (TSM) and particulate organic carbon (POC) in the western Bay of Bengal.

#### MATERIAL AND METHODS

Water samples were collected at surface and at different depths with Niskin samplers during the cruise 193 of R.V. *Gaveshani* (March, 1988). The area of investigation and station locations are shown in Fig. 1. Aliquots (2 l) of sea water samples were immediately filtered on board the ship using preweighed 0.45  $\mu\text{m}$  membrane (Millipore) filters. Filters containing the suspended matter were dried in a vacuum desiccator over silica gel and weighed to an accuracy of 0.01 mg. Filters containing particulate matter and blanks were digested with a mixture of perchloric acid and nitric acid and evaporated to almost dryness. The residues after dilution to 25 ml with HCl (0.1N) were then subjected to trace metal analysis using Perkin Elmer (Model 2380)

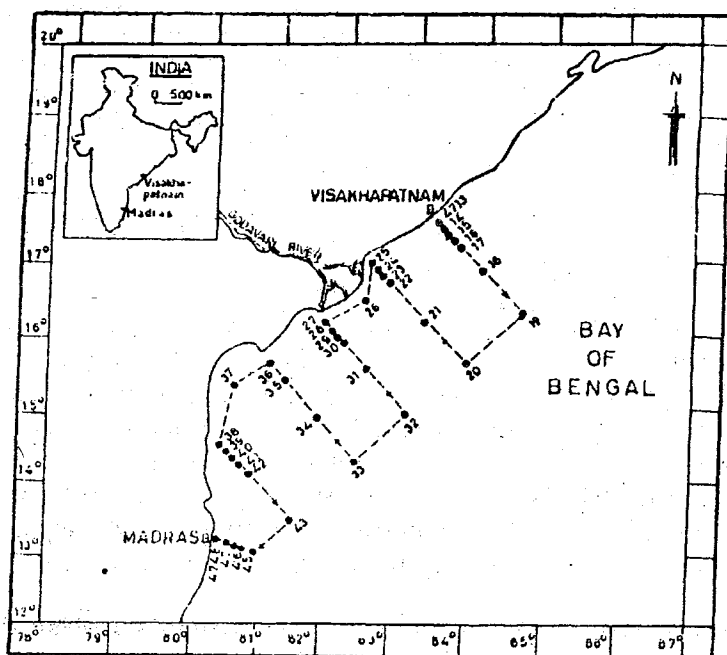


Fig. 1. Area of investigation and location of stations.

Atomic Absorption Spectrophotometer with air-acetylene fuel mixture. The concentrations of trace elements were computed from calibration curves. The precision of the method determined from replicate analyses and expressed in terms of percent coefficient of variation is 10, 8.8, 7.2, 5.5, 5.0, 12.0, 5.0 and 6.8 respectively for Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb. Further, aliquots (2 l) of sea water samples were filtered through GF/C filters on board the ship and POC was determined by wet oxidation with acid dichromate followed by spectrophotometric measurement (Parsons, Maita and Lalli, 1984). Double distilled water and speckpure acids were employed in the analysis.

The particulate trace metal data are presented both as  $\mu\text{g. metal/g}$  (dry weight) of TSM and  $\mu\text{g metal/l}$  of sea water. This is because while the former will help in establishing the composition of the particles and thus contribute to identify their sources, the latter will provide a measure of the total mass of particulate metal in the water sample and thus contribute to assess the relative amounts of dissolved and particulate fractions.

## RESULTS AND DISCUSSION

### *Inshore Waters*

The average concentrations of particulate trace metals, POC and TSM (Table I) in the study area reveal relative enrichment of Mn, Fe, Cu, Zn, Pb and POC in the nearshore, and Ni and Cd in the offshore regions. On the other hand, the concentration levels of particulate Co and TSM are almost similar in both the regions. Relative enrichment of Mn, Fe, Cu, Zn and Pb in nearshore region may be because a major fraction of these constituents are derived from land and river run-off in the particulate form. This is also supported by their occurrence in relatively higher percentage in particulate form when compared with the dissolved form (Table I). On the other hand, the relative enrichment of Ni and Cd in the offshore region can be attributed to their authigenic sources which is evident from their dominant occurrence in the dissolved form when compared with the particulate form, and their scavenging from the water column by hydrous oxides of Fe and Mn. Significant positive correlations between dissolved Ni ( $r=0.67$ ,  $0.56$ ,  $p=99.9\%$ ) and dissolved Cd ( $r=0.80$ ,  $p=99.9\%$ ,  $r=0.42$ ,  $p=99\%$ ) with particulate Fe and Mn respectively in the offshore waters also lend support to this view. Relative enrichment of POC in the nearshore waters can be attributed to the combined effect of the input of allochthonous organic material from the land and higher productivity in coastal waters.

Though the average column concentrations of TSM in nearshore and offshore regions are almost similar, it showed relatively higher concentrations ( $13.75 - 16.05 \text{ mg.l}^{-1}$ ) in the surface samples collected at Godavari river mouth. Rajendran, De Sousa and Reddy (1982) reported high TSM values for surface samples off Godavari ( $0.89 - 7.97 \text{ mg.l}^{-1}$ ) and off Krishna ( $0.75 - 21.89 \text{ mg.l}^{-1}$ ) rivers. Rao, (1985) also reported high

Table I – Average concentrations of particulate trace metals (PTM), POC and TSM in inshore and offshore waters of the Bay of Bengal

Region	Particulate Trace Metals ( $\mu\text{g.l}^{-1}$ )								POC ( $\mu\text{g.l}^{-1}$ )	TSM( $\text{mg.l}^{-1}$ )
	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb		
Inshore waters	1.88-4.75 (3.03)	31.0-173 (88.0)	0.33-0.75 (0.59)	0.25-1.62 (0.89)	1.63-4.25 (2.49)	2.50-15.0 (6.05)	ND-0.25 (0.10)	1.38-7.50 (4.01)	81.0-735 (275)	9.55-19.9 (15.4)
Offshore waters	1.88-3.50 (2.66)	25.0-139 (54.2)	0.25-0.88 (0.55)	ND-1.75 (1.00)	1.00-3.25 (2.07)	2.50-10.0 (4.43)	ND-0.25 (0.12)	0.88-4.13 (2.29)	15.0-474 (169)	12.3-19.5 (15.2)
Percent PTM* in sea water	55	95	-	39	47	62	11	60	-	-

Values in parenthesis indicate averages

(\*) Values computed from the data on dissolved trace metals (Satyanarayana, Prabhakara Murty and Sarma, 1990)

Table II – Particulate trace metal correlation matrix in offshore waters (N = 45)

	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	POC	TSM
Mn		0.47 <sup>b</sup>	0.69 <sup>a</sup>	0.40 <sup>b</sup>	-0.56 <sup>a</sup>	0.27 <sup>d</sup>	-	-0.29 <sup>d</sup>	-0.54 <sup>a</sup>	0.71 <sup>a</sup>
Fe			0.58 <sup>a</sup>	0.76 <sup>a</sup>	-0.51 <sup>a</sup>	0.51 <sup>a</sup>	0.1 <sup>d</sup>	0.25 <sup>d</sup>	-	0.75 <sup>a</sup>
Co				0.64 <sup>a</sup>	-0.42 <sup>b</sup>	0.24	-	-0.31 <sup>c</sup>	-0.44 <sup>b</sup>	0.61 <sup>a</sup>
Ni					-0.55 <sup>a</sup>	0.45 <sup>b</sup>	-0.29 <sup>d</sup>	0.23	-0.26 <sup>d</sup>	0.64 <sup>a</sup>
Cu						0.52 <sup>a</sup>	-	0.41 <sup>b</sup>	0.67 <sup>a</sup>	-0.44 <sup>b</sup>
Zn							-0.22	0.54 <sup>a</sup>	0.70 <sup>a</sup>	0.68 <sup>a</sup>
Cd								-0.14	-	-0.25 <sup>d</sup>
Pb									0.58 <sup>a</sup>	0.63 <sup>a</sup>
POC										0.32 <sup>c</sup>

Level of significance, a = 99.9%; b = 99%; C = 95%; d = 90% .

concentrations of TSM at Godavari and Krishna river mouths ( $122$  and  $2$   $\text{mg.l}^{-1}$ ). A plot of TSM against salinity (Fig. 2) in the surface waters off Godavari river transect (Sts. 4722-25; 4727-30) shows a significant negative correlation ( $r = -0.83$ ,  $p=99.9\%$ ) indicating that a major portion of TSM is derived from the river inputs. The theoretical river water TSM computed from the intercept at zero salinity ( $57$   $\text{mg.l}^{-1}$ ) is in broad agreement with the average ( $122$  ppm; Subramanian, Van't Dack and Van Grieken, 1985) of TSM reported for the Godavari river waters.

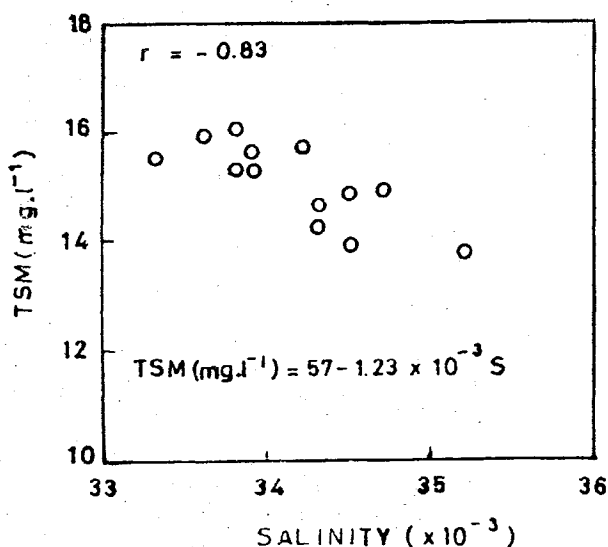


Fig. 2. Scatter plot of TSM versus salinity off Godavari river.

The vertical distributions of particulate trace metals (Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb) in nearshore region, in general, shows relative enrichment in surface when compared with the bottom waters. This may be due to the impact of land derived materials on the nearshore waters. However, no clear trend is evident in the distribution of TSM and POC.

#### *Offshore Waters*

##### Total Suspended Matter (TSM)

The vertical distribution of TSM (Fig. 3a) indicates slight decrease from surface to 500 m followed by an increase at higher depths. Bottom enrichment of TSM can be attributed mainly to the resuspension of sediments by bottom currents. Similar near bottom enrichment observed for waters of eastern continental margin of India has been attributed to the resuspension of bottom sediments (Rao, 1985). The main sources of

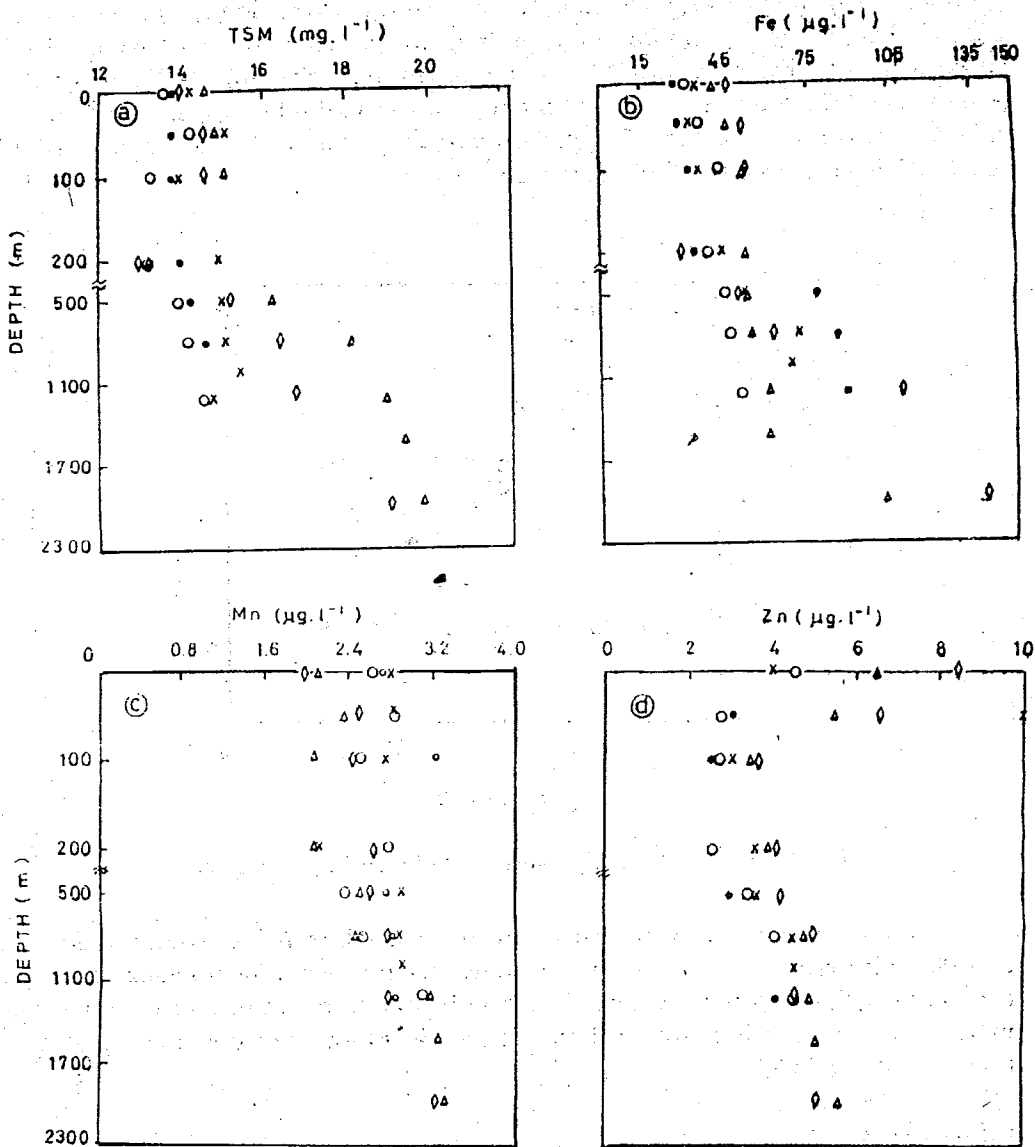


Fig. 3. Depth profiles of TSM and particulate trace metals (Fe, Mn, Zn) in offshore

Table III – Comparison of column concentrations of particulate trace metals ( $\mu\text{g}\cdot\text{g}^{-1}$  dry wt.) with other regions

	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	Ref.
<b>Bay of Bengal</b>									
Inshore	107-315 (201)	2116-12436 (5799)	21-65 (39)	15-118 (58)	90-286 (165)	197-1165 (398)	ND-19.7 (6.93)	100-489 (262)	Present study
Offshore	126-243 (182)	2029-7701 (3552)	15-57 (37)	ND-123 (65)	50-230 (141)	179-664 (298)	ND-17.8 (7.93)	59-274 (153)	
Overall	107-315 (191)	2029-12436 (4596)	15-65 (38)	ND-123 (62)	50-286 (154)	179-1165 (346)	ND-19.7 (7.38)	59-489 (204)	
<b>Bay of Bengal Coastal</b>									
Coastal	10-401 (118)	4506-42408 (18380)	ND-217 (95)	ND-146 (59)	72-197 (134)	644-2853 (1825)	— —	— —	Braganca and Sanzgiri (1980)
Offshore	113-572 (254)	2586-9000 (5547)	ND-251 (71)	ND-83 (28)	ND-398 (106)	511-2816 (1368)			
<b>Andaman Sea</b>									
Coastal	ND-696 (75)	247-44182 (5382)	—	—	ND-521 (125)	81-6160 (1768)	ND-95 (11.4)	ND-1899 (482)	Sanzgiri and Braganca (1981)
<b>Northern Bay of Bengal Coastal</b>									
Coastal	34.3-336 (133)	767-8126 (2456)	ND-66.4 (26.8)	ND-789 (161)	ND-926 (190)	170-1973 (529)	ND	43.2-784 (282)	Satyanarayana, Prasada Reddy Dileepkumar & Ramesh (1987)
Offshore	9.3-103 (56.1)	721-3202 (1738)	ND-63.2 (27.1)	ND-103 (34.2)	ND-24.8 (2.5)	175-991 (366)	ND	44.7-667 (311)	
<b>Indian OceanN (Surface)</b>									
(Surface)	385	—	14	—	202	231	—	44	Chester and Stoner (1975)

TSM in the oceans are river runoff, biological productivity and aeolian dust. However, the contribution from aeolian dust in the Bay of Bengal is negligible (Rao, 1985). Further, the contribution of organic matter (as derived from POC) is also considerably small (2% of TSM). It can, therefore, be presumed that a major fraction of TSM comprises of fine grained inorganic terrigenous matter derived either from the Godavari and Krishna river runoff or from the resuspension of bottom sediments. Significant positive correlations observed in the present study between particulate trace metals (Fe, Mn, Zn, Co, Ni and Pb) and TSM, and among themselves, can be taken as an evidence for their occurrence with fine grained clays and silicate minerals. Rao (1985) also observed the occurrence of fine grained sediments in association with high TSM containing high terrigenous material in the shelf/slope regions of the Bay of Bengal, particularly off river mouths.

### Iron

The depth profiles of particulate Fe (Fig. 3b) in the offshore region exhibit an increasing trend from surface to bottom. Relative enrichment of particulate Fe in the bottom can be attributed either to its precipitation as hydrous iron oxide or as iron oxide coatings on pre-existing particles (Murray and Gill, 1978; Aller, 1980; Lambert, Jehanno, Silverberg, Brun-Cottan and Chesselet, 1981). Significant positive correlations (Table II) of particulate Fe with TSM and other particulate trace metals (Mn, Co, Ni, Zn and Pb) suggests its association with them along with aluminosilicate minerals. This is also supported by the fact that particulate Fe comprises of 95% of total Fe (Table I).

### Manganese

The depth profiles of Mn in the offshore region (Fig. 3c) indicate a decreasing trend from surface upto 200 m followed by a steady increase upto the bottom. Relatively higher concentrations of particulate Mn in the deeper waters and near the bottom when compared with intermediate depths (200 m) can be mainly attributed to the resuspension of the bottom sediment. Significant positive correlations of Mn with TSM and particulate trace metals (Fe, Co, Ni and Zn, Table II) indicate its association with them and occurrence with aluminosilicates and MnO<sub>2</sub> Phases produced during weathering of rocks. A fraction of particulate Mn may also occur in the authigenic form as hydrous manganese oxide.

### Zinc

The vertical profiles of Zn in the offshore region (Fig. 3d) show a decreasing trend upto 200 m followed by a slight increase upto the bottom (2000 m). Its distribution closely resembles that of POC. Enrichment of particulate Zn in surface waters may be related to biological uptake. The uptake of dissolved trace metals (Cu, Mn, Zn, Co and



V) by phytoplankton has been well demonstrated (Riley and Roth, 1971; Knauer and Martin, 1973). It is probable that a fraction of Zn (0.02% of suspended matter) is absorbed by phytoplankton which contributes to a significant amount of POC. This is supported by a significant positive correlation between Zn and POC (Table II). On the other hand, higher contribution (62%, Table I) of particulate Zn to the total in the study region indicates that a fraction of Zn (0.01% of suspended matter) is also of terrigenous origin and occur in association with aluminosilicates. This is also supported by

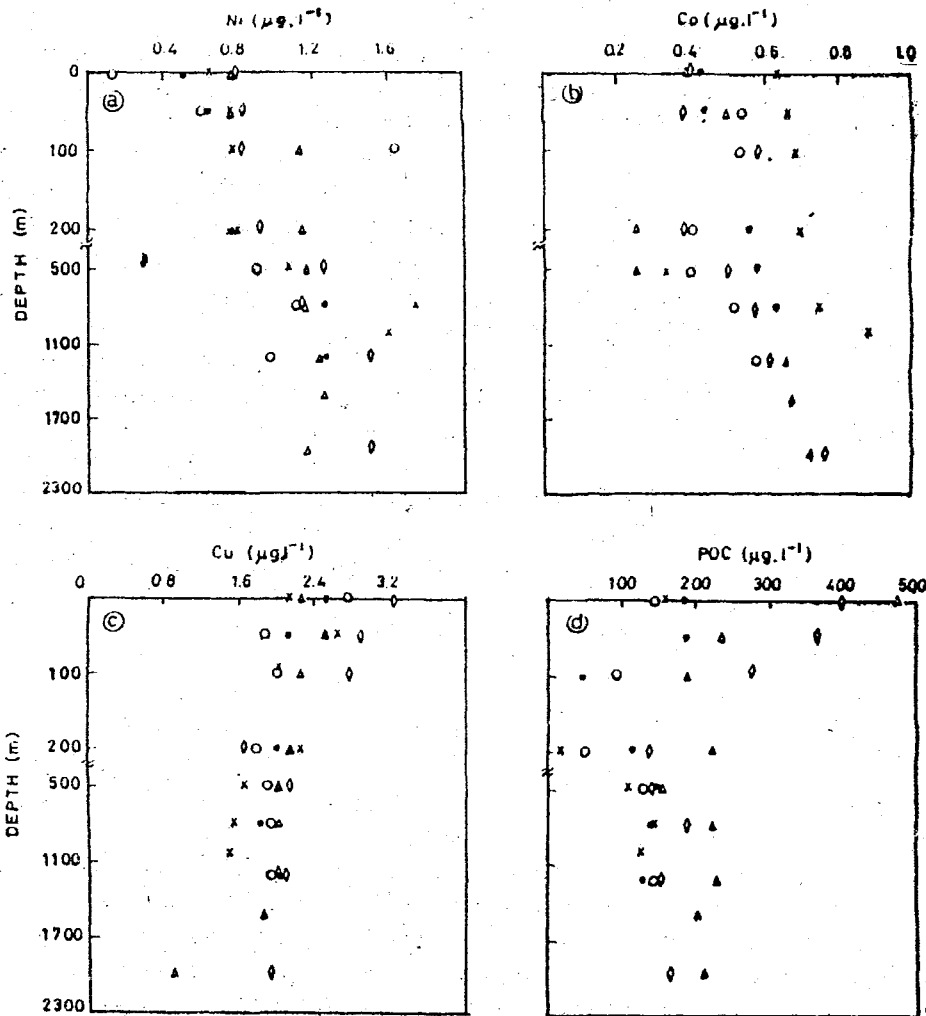


Fig. 4. Depth profiles of particulate trace metals (Ni, Co, Cu) and POC in offshore water of Bay of Bengal (Station No. ● : 4719, ○ : 4720, × : 4721, △ : 4732, ◇ : 4734.)

significant positive correlations observed among particulate Zn, TSM and other trace metals (Fe, and Ni, Table II). Slight increase of particulate Zn in the deeper waters can be attributed to its scavenging by the hydrous oxides of Fe and Mn. Several authors reported scavenging of dissolved trace metals (Zn, Cd, Cu and Co) from seawater (Balistrieri and Murray, 1982) by hydrous oxides of Fe and Mn. Significant positive correlations between dissolved Zn and particulate Fe ( $r=0.74$ ,  $p=99.9\%$ ) and that of particulate Mn ( $r=0.36$ ,  $p=99.9\%$ ) observed in the present study also lend support to this view.

#### Nickel and Cobalt

The vertical profiles of particulate Ni (Fig. 4a) and Co (Fig. 4b) reveal increasing trend in their concentrations with depth. However, particulate Co showed a minimum in the depth interval of 200-500 m. Enrichment of particulate Ni in the bottom layer can be attributed to its scavenging by hydrous Fe and Mn oxide phases. This was supported by significant positive correlations of dissolved Ni with particulate Fe ( $r=0.67$ ,  $p=99\%$ ) and particulate Mn ( $r=0.56$ ,  $p=99\%$ ). Takematsu, Sato and Okabe (1981) have shown that  $MnO_2$  surfaces accumulate Co and Ni especially in regions where Mn precipitation rates are low. Significant enrichment of Ni and Pb in the bottom nepheloid layer in Puget Sound has been attributed to their scavenging by the newly formed hydrous oxide phases of Fe and Mn (Feely, Massoth, Baker, Gendron, Paulson and Crecelius, 1986). In spite of the fact that no significant correlation between dissolved Co and particulate Fe or Mn could be obtained in the present study possibly because of very low and non-detectable levels, close similarity in the distribution patterns of Ni and Co can however, be taken as an indirect evidence for its association with hydrous Fe and Mn oxides. Significant positive correlation of Co and Ni with TSM and particulate trace metals (Fe, Mn and Zn) suggest their association with fine grained terrigenous matter.

#### Copper

Particulate copper profiles (Fig. 4c) indicate a continuous decrease from surface to bottom. Its depth profiles closely resemble that of POC in the upper 200 m. Enrichment of particulate Cu in the top 200 m is related to the biological uptake in the organic fraction. A significant positive correlation between particulate Cu and POC (Table II) also supports this view. Further, lack of correlations with TSM and particulate Fe and Mn indicates its association with phases other than terrigenous and hydrogenous origin. Bottom depletion of particulate Cu may be due to either its removal from TSM by desorption in the water column or its regeneration because of early diagenesis at the sediment-water interface (Bruland, 1983). Enrichment of dissolved Cu at bottom waters reported earlier in the study region (Satyanarayana, Prabhakara Murty and Sarma, 1990) is also in agreement with the above observation.

### Cadmium and Lead

Among the particulate trace metals investigated, Cd recorded very low concentrations (ND -  $0.25 \mu\text{g.l}^{-1}$ ) with an average of  $0.12 \mu\text{g.l}^{-1}$ . This may be due to the fact that it constitutes only a small fraction (11%: Table I) of the total Cd in seawater. As such no definite trend of its vertical distribution could be arrived at in the present study. Significant positive correlations of dissolved Cd with particulate Fe ( $r=0.80$ ,  $p=99.9\%$ ) and particulate Mn ( $r=0.42$ ,  $p=99\%$ ) suggests its association with hydrous oxides of Fe and Mn. Further, it showed no significant correlation with either particulate trace metals or POC indicating its non-association with them.

Though the distribution of particulate Pb showed surface enrichment, its variation with depth was not systematic. It exhibited significant positive correlations with TSM and other particulate trace metals (Cu and Zn) indicating its dominant association (0.03% of suspended matter) with fine grained terrigenous matter. However, a significant positive correlation observed between particulate Pb and POC suggests its partial association (0.01% of suspended matter) with organic matter.

### Particulate Organic Carbon (POC)

The vertical profiles of POC (Fig. 4d) indicate surface enrichment and rapid decrease with depth upto 200 m followed by a slight increase in the bottom waters. Relatively high concentration of POC at surface can be attributed to higher primary production. Its decrease with depth (upto 200 m) may be due to zooplankton grazing and degradation process. Nakajima and Nishizawa (1972) while studying the distribution of POC observed an exponential decrease upto 100 m depth which they attributed to zooplankton grazing (Ca 30%) and degradation process, including bacterial decomposition. Slight changes of POC in deeper waters can be attributed to the combination of two factors namely, (i) variation of surface productivity coupled with processes that transfer organic matter to deeper waters, and (ii) the advection of water masses having different POC contents. Among them, the latter is reported to be the more plausible explanation to account for the variation of POC in deeper waters (Hobson, 1968).

The concentration levels of particulate trace metals (Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb) obtained in the present study (Table II) are in broad agreement with the earlier reports on Bay of Bengal, Andaman Sea and Indian Ocean. However, they are relatively higher in case of Mn and lower in case of Zn and Pb than those reported by Sanzgiri and Braganca (1981) for Andaman Sea. Further the concentration levels of particulate Fe obtained in the present study are much lower than those reported by Braganca and Sanzgiri (1980) for coastal waters of the Bay of Bengal. This is mainly due to the fact that the latter values represent predominantly those of river mouths (Krishna, Godavari, Mahanadi and Ganges) where the concentration levels of TSM as well as particulate Fe are much higher than those of coastal waters.

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